Modifications in Fluorocarbon Bladder Structures in Improving Flexibility and Impermeability

by

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Abstract

Modifications in fluorocarbon bladder films involve optimizing the merits of high molecular weight, high melting Teflon TFE and its lower molecular weight, lower melting copolymer Teflon TFE fluorocarbon resin. The former provides the basis or matrix for rubbery or viscoelastic endurance along with high build-up, while the latter provides the low temperature flexing and maximum impermeability. The combinations or proportions can be pre-assessed by stress-strain analysis of the tensile curve. Optimization then becomes a matter of screening the raw materials that will assure retention of high molecular weight and minimum level of crystallinity. Improved bladder films and particularly reproducibility of high performance can be surveyed by this analytical and correlative investigation.

I. Introduction

Fluorocarbon polymers comprising polytetrafluoroethylene and its copolymer with hexafluoropropylene, commercially available as the proprietary Teflon (R) TFE and FEP resins and shown structurally in Figure 1, have historically since the inception of the aerospace program from the early Gemini ventures proven their utility in the design and production of positive expulsion bladders. (1). The success of the "Teflon" derived bladders in over scores of orbital and interplanetary projects continues to rank the fluorocarbon polymers high on the preference list over various metallic, elastomeric and miscellaneous composite innovations and structures. Despite some shortcomings in comparison with other materials of construction, the continued dependence upon the Teflon fluorocarbon polymers will prevail of necessity for much of the forseeable future.

As with any material of construction adopted for space systems, the problems of efficiency

reliability, and consistency require an inordinate amount of continued development. Unlike conventional commercial and industrial applications those for space science and technology will continue to demand the ultimate, sophisticated refinements in the basic fluorocarbon materials. Such being the case, we have taken the viewpoint that the aerospace materials industry should recognize the intrinsic properties and merits of the fluorocarbon constructions to be optimized much like metals and non-metallic materials have been improved by ever-narrowing and selection of their unique features. In other words, optimization rather than total substitution may be more prudent considering the past ten years of already proven, unmistaken performance of Teflon propulsion bladders. The question then arises where can one seek this optimization and by optimization we mean putting together the best features of the individual fluorocarbon polymers. This presentation therefore attempts to point out several
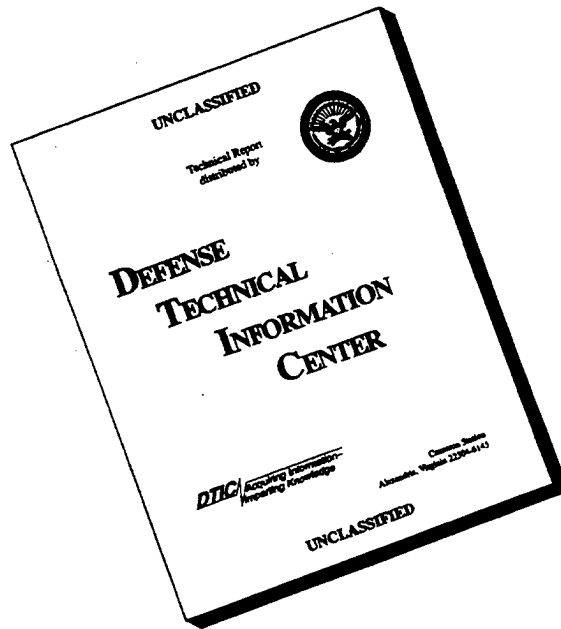
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areas of needed understanding of the fluorocarbon polymers and the manner in which the current technology and evaluation may be directed into ever-improving levels of reliability and performance.

Basic Characteristics of Fluorocarbon Polymers.

Basically, the Teflon TFE and FEP polymers (2,3) are unique for the bladder programs on the following counts:

(a)   chemical inertness

(b)   adequate mechanical strength

(c)   flexibility, and

(d)   light weight.

It is indeed the combinations of these three principal attributes that fit the needs for bladder constructions.

Molecular and Related Characteristics.

The two grades of Teflon, TFE and FEP polymers as depicted in Figure 1 differ in several respects as shown in Table 1, but notably in regard to melting point and chain length or molecular weight. The higher melting TFE polymer coalesces by sintering under viscoelastic restraining (4), whereas the lower melting FEP copolymer coalesces by viscous fusion.
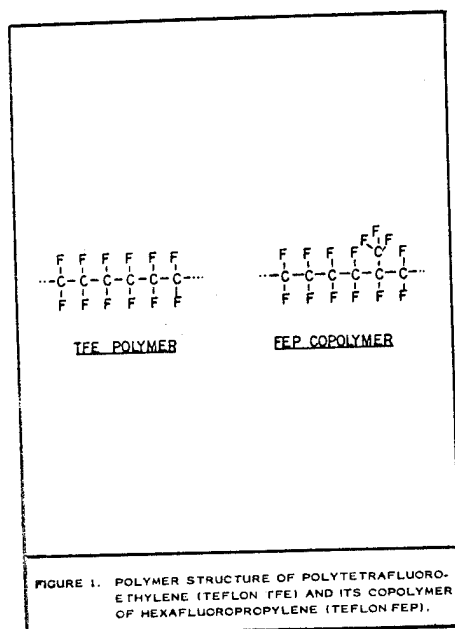
FIGURE 1.   POLYMER STRUCTURE OF POLYTETRAFLUOROETHYLENE (TEFLON TFE) AND ITS COPOLYMER OF HEXAFLUOROPROPYLENE (TEFLON FEP).

Table 1.   Summary of Comparative Characteristics TFE and FEP Polymer

Property	TFE	FEP
(A) Molecular and Related Characteristics		
(1) Particulate structure, micron	0.2	0.1
(2) Melting point, °C.	327	265
(3) Melt viscosity	cal0"	cal0"
(4) Molecular Weight	$6-10\times10^6$	10^4-10^5
(5) Coalescing mechanism	Sintering	Melting
(6) Crystallinity (after coalescing)	45-75	25-35
(7) Thermal Stability	Stable	Less stable
(B) Engineering Properties (Crystallinity dependent)		
(8) Modulus, tensile, lb/sq.in.	55,000-70,000	70,000-90,000
(9) Flex life MIT(5-7 mil)	101	$1-3\times10^5$
(10) Permeability	High	Low
(11) Cold crack	Fair	Good

A notable feature distinguishing these two grades of fluorocarbon polymers is the crystallinity level attained after coalescing into the fabricated form.   Whereas the higher molecular TFE crystallizes to high level of crystallinity, the lower molecular weight FEP copolymer attains a considerable lower degree of crystallinity.   Coupled with the molecular weight variability as regulated by the parent resin supplier (DuPont), the attribute of crystallinity can have a highly significant impact on the engineering or mechanical properties. . Table 2 summarizes the changes due to increasing molecular weights and crystallinity (5) especially in flexural fatigue and permeability which are highly critical to optimal bladder constructions.   In the usual processes of coalescing to molded or film constructions, properly restricted thermal exposure plays a significant role in minimizing excessive depolymerization which lowers the molecular weight and as a consequence gives rise to increased crystallinity.

Table 2.   Effect of Molecular Weight and Crystallinity on Engineering Properties of TFE Polymer (5).

Property	Maximum Changes due to Increase In:	
	Molecular Weight	Crystallinity
Flex life	+100x	-100x
Flex modulus	(0) negligible	+5x
Tensile Impact	(0) negligible	-15x
Yield stress	(0) negligible	+15%
Permeability (CO_2)	(0) negligible	-30x

For this reason the fabricator's role in selecting the raw material and applying the correct coalescing technology is an extremely important and critical one. Molecular changes from raw material to finished bladder construction is an important technological facet vested upon the fabricator's proprietary technology.

Flexible Characteristics.

The flexible structure as required for bladder-collapse during liquid expulsion is the least understood merit of the fluorocarbon materials as a class. Teflon fluorocarbon is often mistakenly and improperly assessed as a rigid plastic very much like one would categorize acrylics, nylon, epoxy-resins cured phenolics and so on which are endowed with a stiffness or modulus of elasticity (6) ranging from 0.25 to 1.25 million pounds per square inch. Rubber and synthetic elastomers, depending upon level of vulcanization and reinforcement, run from as low as 500 to 50,000 pounds per square inch; hard rubbers of course can be cured to rigid plastics or plastic-like materials. In the scale of modulus of elasticity as shown in Figure 2, Teflon more nearly approximates the cured rubber range with modulus ranging from 40,000 to 90,000 lbs./sq.in. In our development efforts, we have continually attempted to adapt the raw materials to this modulus range holding down the high modulus or stiffness as much as possible and consistent with the critical requirements in bladder flexibility.
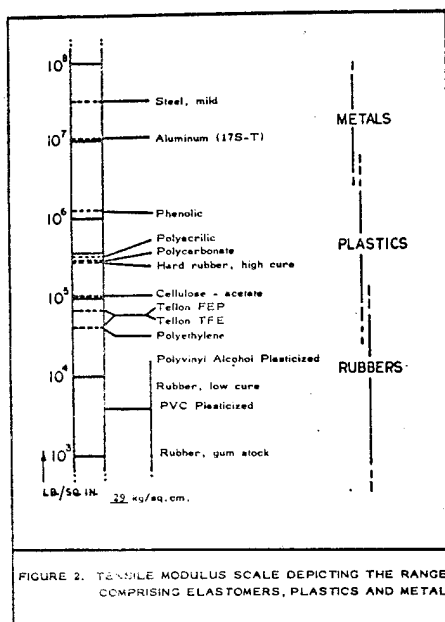
Viscoelastic Characteristics.

Since rubbers are basically viscoelastic materials, that is, inherently endowed with elastic or recoverable component along with viscous deformation, we further take the view that some component of the fluorocarbon can be exploited with a rubberlike behavior. As will be developed in ensuing section on stress-strain characteristics, we view the high molecular weight TFE polymer as a viscoelastic engineering material in contradistinction to being rated a rigid polymer or plastic. Our view further emanates from the basic characterization of this polymer by Lontz as being coalesced or sintered by viscoelastic mechanism.

II. Technological Involvement.

It is first necessary to recognize that the preference or selection of fluorocarbon polymers for the expulsion bladders involves three distinct areas of product technology. In our Systems Analysis shown in Figure 3, this first involves the systems requirements, secondly, the fabrication technology, and thirdly the raw material specifications or molecular characteristics. Each of these three areas has imposed upon it certain limitations or boundaries which may or may not be attainable depending upon the availability of the raw materials, and their proper processing through the next stage for the specific systems requirements.

FIGURE 2. TENSILE MODULUS SCALE DEPICTING THE RANGE COMPRISING ELASTOMERS, PLASTICS AND METAL
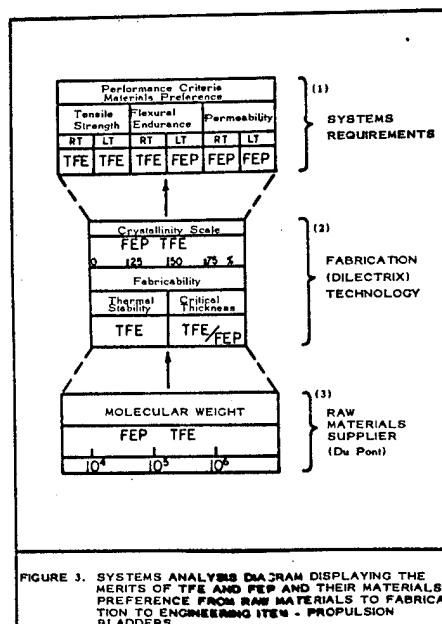

FIGURE 3. SYSTEMS ANALYSIS DIAGRAM DISPLAYING THE MERITS OF TFE AND FEP AND THEIR MATERIALS PREFERENCE FROM RAW MATERIALS TO FABRICATION TO ENGINEERING ITEM - PROPULSION BLADDERS.
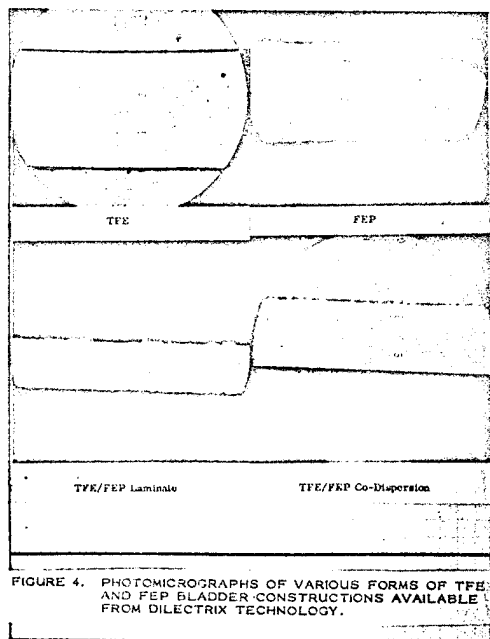
Systems Requirements.

Among the various criteria, the three primary requirements correlatable to moleculer characteristics include the following:

(a) Tensile (stress-strain) properties

(b) Flexural endurance, and

(c) Permeability.

In each of these areas it is seen that the preference between the TFE and FEP polymers varies depending whether the performance rating involves ambient room temperature (RT) on the one hand or low temperature (LT) on the other. It is therefore evident that both polymers need to be used in either one of the two possible bladder film constructions, namely,

(a) alternate laminate (composite) film structures or

(b) mixtures of TFE and FEP applied from co-dispersion.

Variations of these constructions are shown in Figure 4, reported in an earlier progress report (7), as new possible approaches toward up-grading bladder film utility and endurance. More, particularly, these varied constructions were devised as one practical approach to optimize the individual merits of each of the two grades of resins.

FIGURE 4. PHOTOMICROGRAPHS OF VARIOUS FORMS OF TFE AND FEP BLADDER CONSTRUCTIONS AVAILABLE FROM DILECTRIX TECHNOLOGY.

Fabrication Technology.

To achieve these variations shown in Figure 4 and their continued development or extensions, the proprietary fabrication technology had to be adjusted in the light of (a) variable thermal stability and (b) marked differences in the critical thickness (8) of the resins applied from dispersions.

Thermal degradation poses little problem for the TFE polymer (M.P. 327°C), but the lower melting polymer (M.P. 260°C), preferred for its low temperature flexural endurance and lower permeability, imposes restrictions on thermal schedules. It is evident that thermal stability of the raw material FEP can be a significant factor and needs further improvement for either construction and particularly for the codispersions which are discussed in an ensuing section. Degradation of FEP affects the flexural endurance as our current efforts indicate.

Applied from aqueous dispersions, the TFE and FEP resins have different levels of permissible coating thickness and build-up. The more that one applies the FEP the lower becomes the permissible thickness, suggesting that raw materials improvement can become an important factor in upgrading the fluorocarbon bladder film composites. In the meantime, circumventous means are being adopted to exploit the maximum and selected raw materials batches with our own intramural screening.

Raw Materials.

As implied above, the proprietary (DuPont) raw materials determine the fabrication technology aimed toward (a) preserving the maximum molecular weight and (b) maintaining an optimal balance of crystallinity for low permeability on the one hand and high flexural endurance on the other. Each batch or shipment is checked extensively before selection for bladder film production with an array of intramural pre-checks. Variations in raw material despite the commercial specifications (2,3) are being narrowed with time and at best depend upon systems performance feedback. Meanwhile, efforts toward characterizing the raw material TFE and FEP and their co-dispersions are in progress with detailed tensile profile studies to monitor bladder films for the ensuing flexural endurance and permeability.

III. Tensile (Stress-Strain) Characterization.

The use of TFE-FEP co-dispersion makes it incumbent to catalog or otherwise characterize the stress-strain profile as a prelude to more involved and detailed flexing tests. The co-dispersions of these two dissimilar polymers, coalesced by melting of FEP and sintering of TFE into bladder film at their optimal temperature ranges, has been found to result in markedly different stress-strain curves. Figure 5 indicates the pure TFE and FEP tensile stress-strain with their normally low and high levels of crystallinity. Particularly noteworthy is the effect of crystallinity on the profile with TFE and the presence of a significant viscoelastic yield strain up to at least 20 and possibly 50 percent strain attainable with low crystallinity bladder films. Moreover, under certain casting schedules the TFE profile shown in Figure 5 includes a definite delayed or restraining modulus (region A to B) estimated at about 1000 lb/sq.in. or roughly one-fifth to one-eighth of the initial modulus. According to Lontz' concept (4) this initial and delayed strain region reflects a viscoelastic or rubbery region with measurable retardation constants or time restraint. Our fabrication efforts have utilized this initial and delayed strain as a basic TFE molecular requirement to be maintained as FEP is incorporated to optimize low permeability and low temperature flexural endurance.
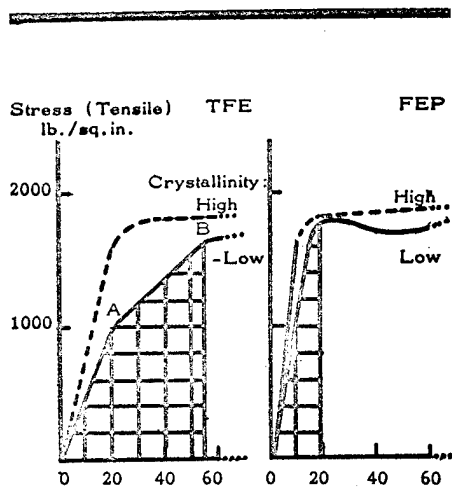
The progressive addition of FEP up to 50 percent gradually diminishes this viscoelastic recoverable strain region as depicted in Figure 6. The stress-strain profile was taken from Instron charts at high chart speeds up to 50 inches per minute in order to accentuate the early strain component; ASTM Procedure 1457-62-T was used at a strain rate of 2 inches per minute. From these profiles it is evident that the progressive increase in the FEP level shifts the combined instant and delayed viscoelastic component into lower yield strain levels approaching that of pure (100 percent) FEP. It is clear that one can adjust the TFE/FEP co-dispersions to the most optimal systems properties or merits by monitoring these profiles with changes in raw material molecular attributes.
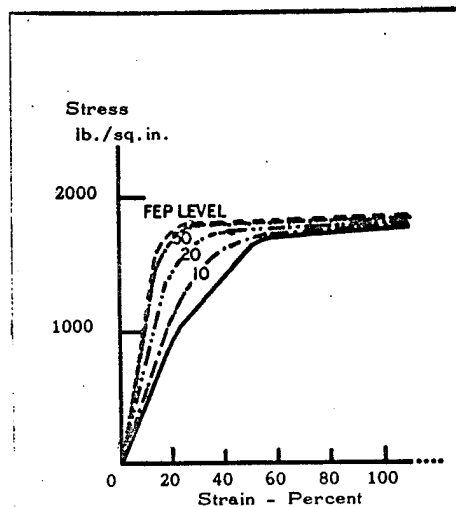

FIGURE 6. TYPICAL STRESS-STRAIN PROFILE OF TFE AND FEP BLADDER FILMS OF VARIED PROPORTIONS PREPARED FROM CO-DISPERSIONS.

IV. Flexural Endurance.

Concommittantly with the above tensile characterization, two types of flexural qualifications have been carried out in relation to (a) fabricating, casting processes (9) and (b) raw materials (TFE and FEP) acceptance for the ultimate bladder films. Two methods of flexural endurance have been adopted, each having its own features and established validity and applicability, both involving folding or creasing of the film.

FIGURE 5. TYPICAL STRESS-STRAIN PROFILE FOR HIGH AND LOW CRYSTALLINITY BLADDER FILMS FROM PURE TFE AND FEP.

M.I.T. Folding Endurance.

Originally developed at the Massachusetts Institute of Technology, this tester (10) has been adopted as standard by the American Society for Testing Materials, designated by the procedure D-2176-63-T and D202, and the Technical Association of the Pulp and Paper Industry, designated TAPP-1-T423-M50. In this test, the pliable test samples, equivalent to the bladder film in stiffness, are repeatedly folded to failure under a tensile load in the machine shown in Figure 7, to an angle of 135° in both directions at the rate of 175 double folds per minute until the sample is severed at the crease. An integral counter, which records the total number of double folds or cycles, is automatically stopped at the instant the specimen fails. The test is usually conducted at room temperature which was used in our qualification of raw materials and bladder preparation schedules.
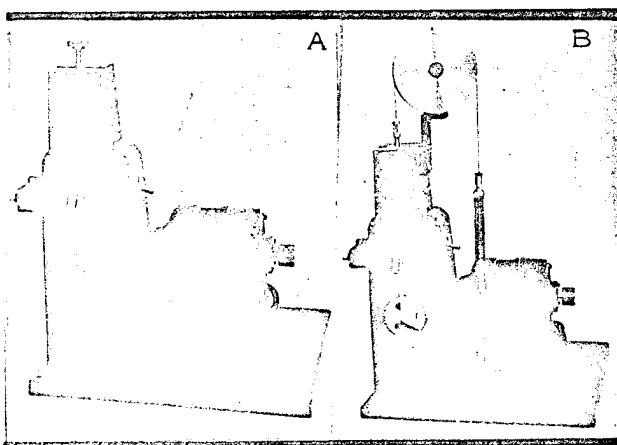
most industrial or commercial end-products, but need considerable narrowing for the more limited and specialized bladder film constructions. The endurance test decreased with decreasing molecular weight and with increasing crystallinity. (5) The latter needs to be kept high for high permeability but at the same time needs to be kept in bounds for maximum flexural endurance. Molecular weights are controlled by the supplier but severity in thermal melting or sintering will cause degradation (11) to lower melting entities and consequently higher crystallinity and in turn lowered flexural endurance. This recounting of the molecular-crystallinity implication is important for emphasizing the close coordination needed in the overall effort depicted in Figure 3. The M.I.T. flex test, however, is more product-oriented for characterization and not for in-service pre-testing, especially for more complex crease-folding which is more generally encountered in actual propulsion services.
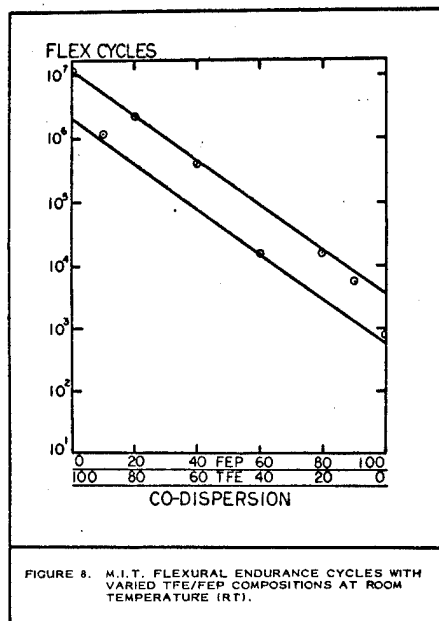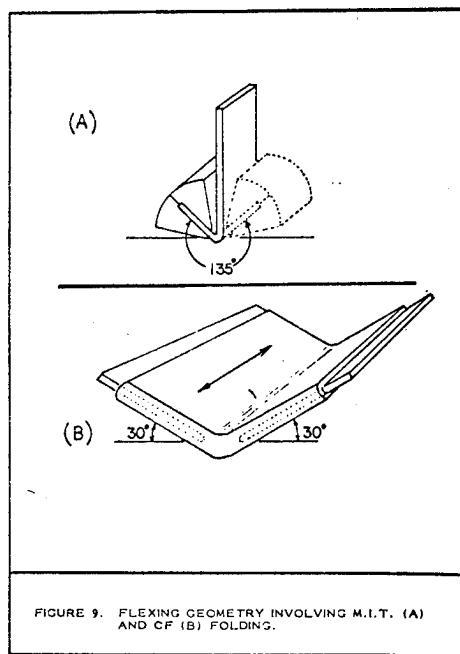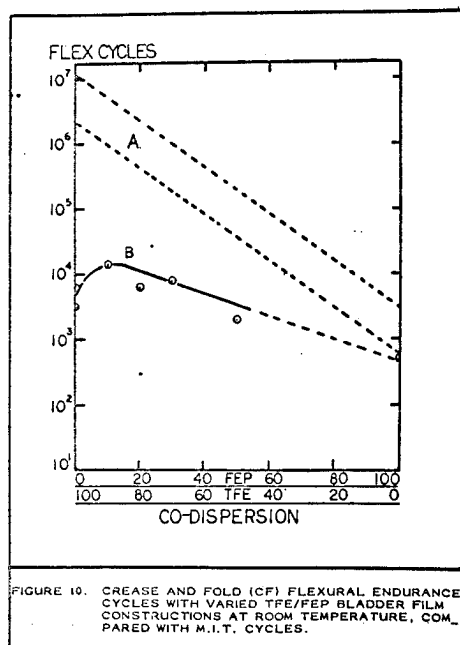
Figure 7. M.I.T. Folding (Flexural Endurance Tester for Paper (A) and Plastics, (B).

This folding endurance test is particularly sensitive to molecular weight and crystallinity. Figure 8 indicates the range of flexural cycles to break differentiating the high flexing high molecular weight TFE (10^7 cycles) from its lower molecular weight FEP copolymers (1 to 3×10^4 cycles) along with several intermediate polymer admixtures, made from co-dispersions. The figures also indicate that the progressive admixture of FEP decreased the flexural endurance cycle.

This test is invaluable for our intra-mural control over the bladder film production on the one hand and screening preferred lots of raw material, TFE and FEP, whose range of specifications is generally acceptable for

FIGURE 8. M.I.T. FLEXURAL ENDURANCE CYCLES WITH VARIED TFE/FEP COMPOSITIONS AT ROOM TEMPERATURE (RT).

Crease and Fold (CF) Endurance.

In order to more nearly replicate the collapse-fold in a propulsion bladder several interested agencies have mutually devised and adopted a cyclic test shown schematically in Figure 9 along with the M.I.T. fold geometry. This test is conducted at room temperature and at -11.2°C (12°F) which is the solidification point of one of the standard propellant fuels.

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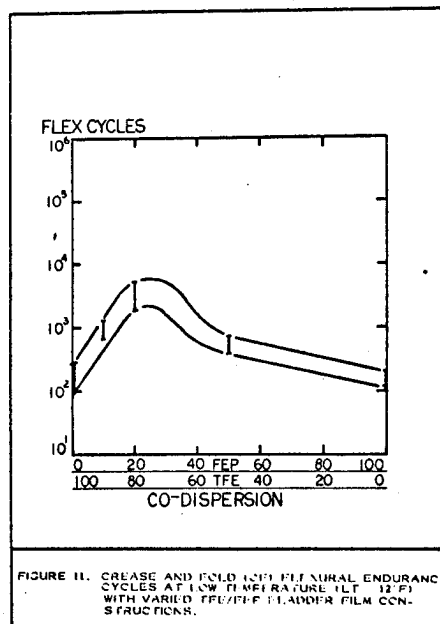FIGURE 9. FLEXING GEOMETRY INVOLVING M.I.T. (A) AND CF (B) FOLDING.

The present state of the co-dispersion technology in regard to flexural endurance at room temperature is shown schematically in Figure 10, again using both pure TFE and FEP with an initial series of TFE/FEP mixtures. At room temperature the M.I.T. and CF endurance pattern follows quite closely that of the M.I.T. flex tester. In the case of the CF test we see now at the room temperature conditions an optimization at approximately 10-20% of the flexural endurance improved by the FEP on the TFE.

When the CF test is conducted at -11.2C (12°F) as shown in Figure 11, we can see a similar optimization at the same 10-20% level of FEP incorporation into the TFE basic matrix. This unique co-dispersion composition range is under further investigation as is the refinement of the CF test eventually for formal submittal to Round Robin assessment into a formalized spec. test hopefully involving several independent laboratories. In our experience we find that the nature of the flex failures and fractures vary considerably. The CF test lacks the quantification at failure whereas the M.I.T. testing is designed to stop at total failure. Each of these tests have their respective merits and disadvantages and they should be kept within the systems evaluation scheme.

The test reproducibility, particularly with regard to the intensified crease line, has yet to be established with detailed scanning of the fracture at higher magnification.

In addition, the CF test as presently run is not altogether environmentally duplicated on co-dispersion film structures being done in air rather than in the propellant system. The chemical nature of the propellant and its surface energetics adjacent to the creasing, straining film has yet to be checked out. There have been instances of such physical-chemical interactions under stress that change the nature of the fracture either ameliorating the strain effect or intensifying it.

FIGURE 10. CREASE AND FOLD (CF) FLEXURAL ENDURANCE CYCLES WITH VARIED TFE/FEP BLADDER FILM CONSTRUCTIONS AT ROOM TEMPERATURE, COMPARED WITH M.I.T. CYCLES.

FIGURE 11. CREASE AND FOLD (CF) FLEXURAL ENDURANCE CYCLES AT LOW TEMPERATURE (LT -12°F) WITH VARIED TFE/FEP BLADDER FILM CONSTRUCTIONS.

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Mechanism of Flexural Failure.

Efforts are currently in progress to ascertain what molecular and fine structure factors contribute to or repress flexural fatiguing and failure. Lontz (6) has already indicated in the case of TFE flexing the onset of amorphous component along with micro-voids to a measurable level in biological medical failure. It is expected that this approach involving phenomological study is necessary at least to gain some rationale if not a definitive mechanism that would accord further guidance to the interdiffusion of the two dissimilar, even though chemically related, polymers. These efforts are scheduled for continued investigation.

V. Permeability.

As a critical systems materials requirement, complete or minimal permeation to the liquid propellants, notably nitrogen tetroxide (N_2O_4) and hydrazine (N_2H_4), is the ultimate goal or merit. However, as with any organic barrier material permeation and diffusion is inevitable. As implied in the systems scheme depicted in Figure 3, permeability or its minimal levels is dependent upon the fabrication imposed and basically upon the two raw materials, TFE and FEP polymer, made available in a range of molecular weights and thermal stability.

The bladder films were tested for N_2O_4 permeability using titrametric analysis of the permeant gas swept by helium into a cold trap by the procedure devised by Vango (13). Figure 12 depicts a typical range for the co-dispersion mixtures, along with a FEP/TFE laminate construction. It will be seen that at approximately 20 percent loading a marked improvement in impermeability (i.e., decreased permeation constants) is attained to a 50/50 TFE/FEP codispersion level which approximates that of pure FEP film. Coupled with the maximal flexural at the 20 percent level, it now becomes apparent that for increased permeability the systems choice will have to be somewhere between 20 and 50 percent FEP in TFE. One must consider likely reservations on the more narrowed range as additional data accumulates on definite assignment of molecular weights and crystallinity and its mophological forms.
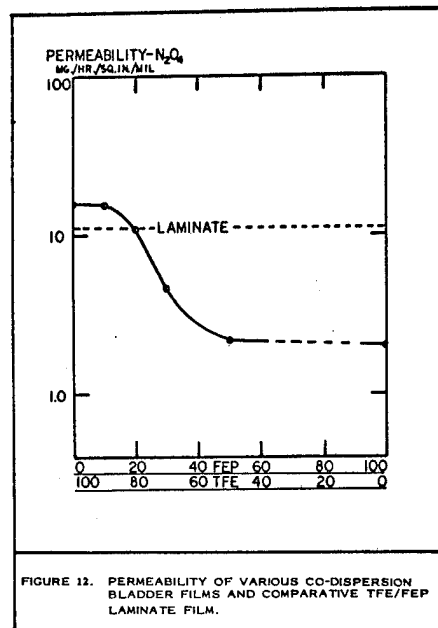

FIGURE 12. PERMEABILITY OF VARIOUS CO-DISPERSION BLADDER FILMS AND COMPARATIVE TFE/FEP LAMINATE FILM.

Summary and Conclusion.

The proven performance of fluorocarbon bladder films for propulsion systems is approaching the development stage where the merits of the high molecular weight, high melting TFE polymer can be further composited with its lower melting analog, FEP polymer, which can provide higher impermeability, and possibly improve low temperature flexural endurance. The development effort is now involving selective use of the polymers in both composition ratios but also more defined raw material characteristics. The nature of the stress-strain profile and the correlative performance in actual flexural service, including the full environment now needs to be pursued for more definitive and mechanistically plausible systems engineering guidance.

Acknowledgement

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Biography

Mr. Petriello is a graduate Chemical Engineer having received his degree from Pratt Institute in 1943. He founded the Dilectrix Corporation in 1950 and has specialized in fabrication and the application of fluorocarbons and associated materials. He is a member of the AIAA, SAMPI, SPI, Vacuum Coaters Society, American Ordnance Association and ASTM. He has been granted 7 U.S. Patents and is co-inventor on 4 pending applications.